High-Throughput Combinatorial Development of High-Entropy Alloys for Lightweight Structural Applications

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Intermolecular, Inc.

June 6, 2017

Project ID #
LM109

Overview

Timeline

- Project start date 10/1/2015
- Project end date 9/30/2017
- Percent complete 75%

Budget

- Total project funding $3,166,346
  - DOE share - $2,533,076
  - Contractor share - $633,270
- Funding FY2016 = $1,562,062
- Funding FY2017 = $971,014

Barriers

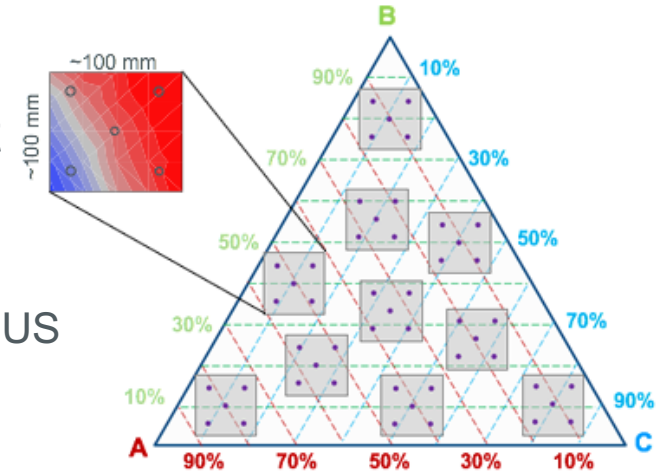
- Barriers addressed
  - **Cost:** not greater than 5$/kg
  - **Performance:** leading to 50% reduction in primary metal weight in automobiles by 2050
  - **Predictive Modeling**: validate potential for high throughput tools and methodologies in alloy development

Partners

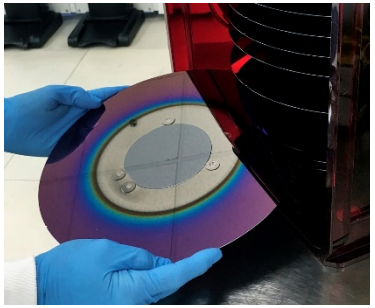
- Project lead – Intermolecular
- Collaborators
  - N.C. State University
  - Ohio State University
  - Arconic
  - General Motors

Relevance

- Overall objectives:
  1. Validate Intermolecular's high-throughput experimentation (HTE) approach to lightweight alloy discovery development.
     - Combinatorial thin-film deposition (discovery) PLUS
     - Advanced alloy modeling combining both theoretical and observational models
  2. Demonstrate the viability of low-density, high-entropy alloys (LDHEAs) as a lightweighting approach for vehicle applications to meet goals in the DOE-VTO MYPP. The Multi-Year Program Plan is the guiding document for funding VTO projects.
     - HEAs are specific concentrated multinary alloys
     - Potential for higher specific yield strength (SYS) than traditional alloys
     - Design flexibility for corrosion and processing
     - Large, unexplored composition space



Isothermal slice of a 3-element phase diagram



Typical gradient film on substrate

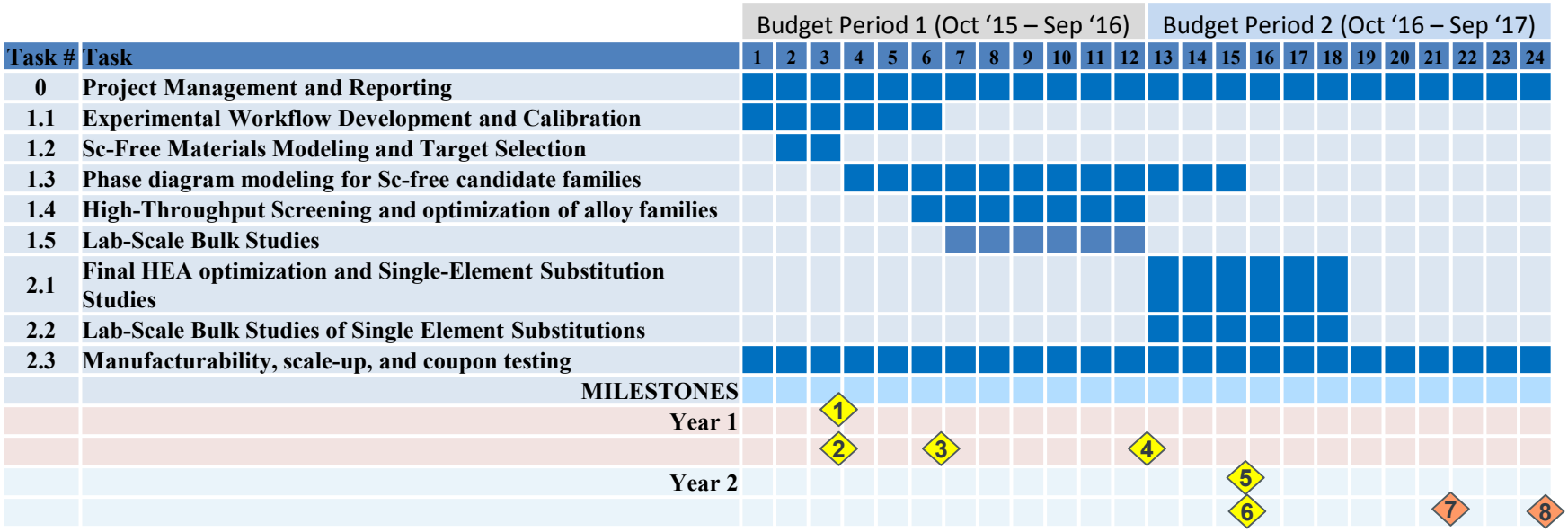
Relevance for addressing barriers

- Cost and Performance
  - Goal: achieve the SYS of a Ti alloy for the price of a Mg alloy
    - "Stronger than Ti, cheaper than Mg"
- Modeling
  - From 150 billion possibilities to 1 alloy meeting targets
  - Must be fast and robust to new input

Performance Targets

Parameter	BP1 Target	BP2 Target
Yield Strength (MPa)	≥1500	≥3000
Mass Density (gram/cm3)	≤5	≤5
SYS (MPa cm3/gram)	≥300	≥600
Cost ($/kg)	≤$5/kg	≤$5/kg
Performance Cost Index (PCI) (PCI of 1 equals the same material cost as equivalent strength steel)	≤1.01	≤0.72

Approach

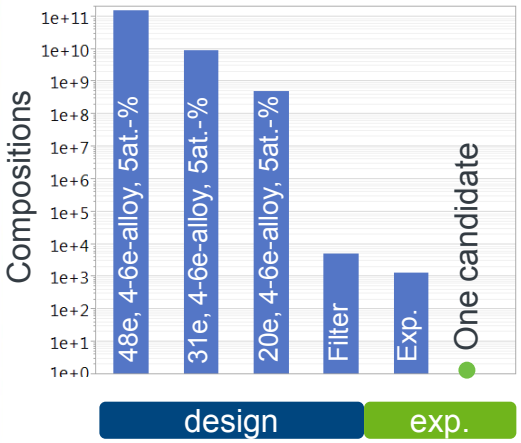


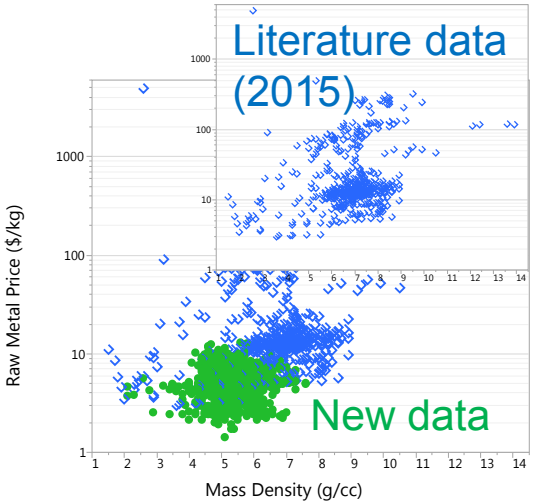
Complete | **In Progress**

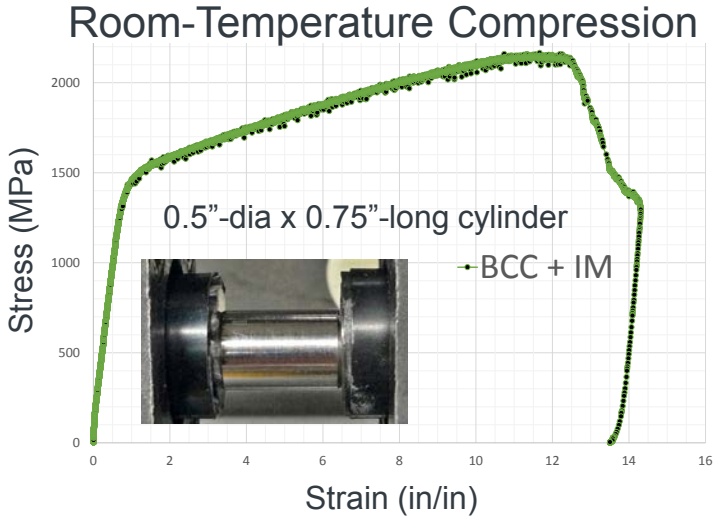
Milestone	BP	Description
1	1	HTE workflow complete and ready for alloy gradient fabrication
2	1	Initial alloys deposited
3	1	Calibrated phase diagrams for all candidate alloy families
4	1	One or more LDHEA meets performance targets; HTE results within 10% of small bulk results
5	2	Calibrated phase diagrams for all single-element substitution alloys
6	2	At least 1 thin-film composition meeting all targets
7	2	At least 1 bulk sample meeting all targets
8	2	Final coupon testing complete

Executive Summary

- Started from 150 billion compositions and found so far one potential candidate
- Increased existing HEA database (~10yrs) by 3x in 18 months with focus on low-density HEA (LDHEA)
- Found one alloy with specific compressive yield strength = 229 MPa x cc/g, which would allow 40% weight reduction for connecting rod (in ICE). RT & hot tensile testing, followed by optimization, RT & hot fatigue testing, and corrosion testing are scheduled.
- Final efforts started to find ductile LDHEA with density <5.5g/cc







Technical Accomplishments and Progress – Project Design

INTERMOLECULAR

High-Throughput Material Design

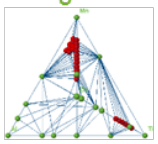
Market Needs

1. Strength
2. Price
3. Density

Phenomenological Alloy Design

1. HEA experimental database
2. Phase diagrams (experiments & CALPHAD)
3. Selection rules

Simple phase diagrams



Feedback

Validate Prediction

Puck fabrication & characterization

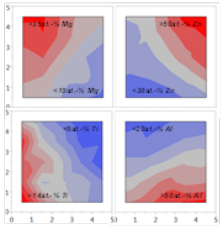
1. Fabrication (melt, mill) & anneal
2. Microstructure (XRD, SEM/EDS)
3. Micro-hardness & indent images

Feedback

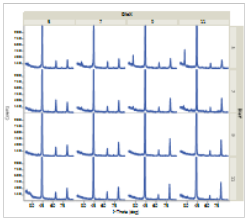
Feedback to improve transfer

High-Throughput Experimentation to identify trends with composition

Composition map



XRD Map



1. Phase space mapping with XRD
2. Hardness mapping with nano-indentation

Feedback

Small Bulk Samples verification, optimization, tests

Feedback

Large Bulk Samples verification, optimization, tests

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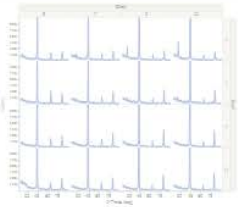

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Electronegativity trumps all

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HEA Database

- **Single Phase Solid Solution (Y/N)**
- 1,490 exp. points (24 sources)
- All process conditions
- Filtered to >550 data points

Parameters

- 91 parameters
- Thermodynamic, geometric, electronic, density, and price
- *1 input table for 48 elements*
- *3 binary enthalpy matrices*

80% parameters significant (p-value <0.05)

- END ranks 1st in significance for *single-phase disordered solid solutions (SPSS)*
- ASD (based on CN = 12) ranks 2nd
- Entropy/enthalpy ratio achieves p-value = 0.02
- Larger probability of SPSS for higher mass density
- Larger probability of SPSS for less elements

ID	Parameter	p-value	t-statistic
1	END (Allred-Rochow scale)	8.E-36	-14.3
6	ASD (CN = 12)	1.E-25	-11.5
22	Mass Density	1.E-11	7.2
35	Number of elements	2.E-08	-5.9
46	Young's Modulus	7.E-07	5.1
67	Valence Electron Concentration	2.E-04	3.9
72	Entropy/Enthalpy Ratio	2.E-02	2.4

$$\sqrt{\sum_{i=1}^{n} c_i(\chi_i - \overline{\chi})^2}$$

END
(electronegativity difference)

$$\sqrt{\sum_{i=1}^{n} c_i(1 - r_i/\overline{r})^2}$$

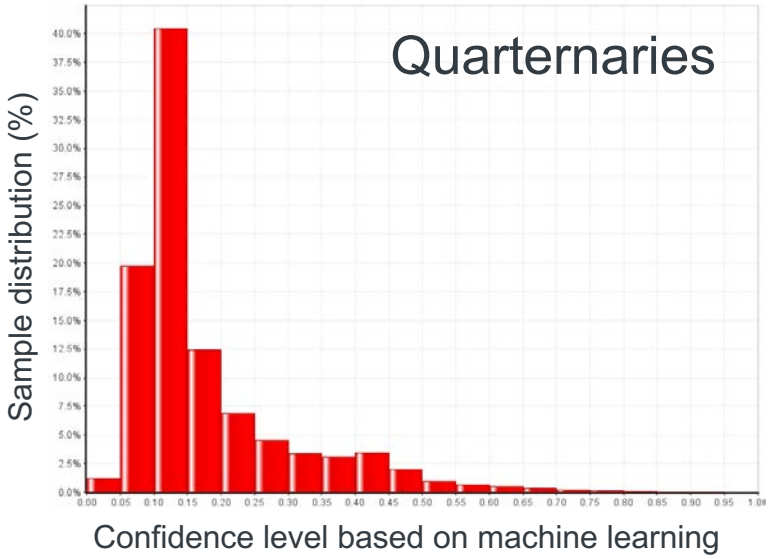
ASD
(atom size difference)

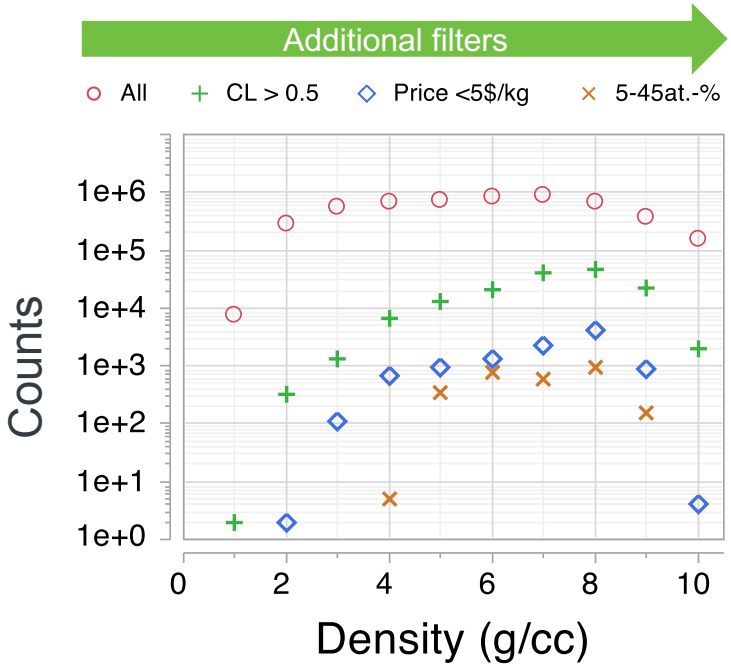
$$\frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}$$

Ω
(Entropy/enthalpy ratio)

Machine Learning shows low number of SPSS candidates <5g/cc

- Machine learning, based on HEA database and parameters, used to guide alloy design for single-phase solid solutions (SPSS)
- Results shown below for quarternaries starting from 31 elements, with each element in range 5-85at.-% in steps of 10at.-%
- ~3% of population with confidence level >0.5 for SPSS (all mass densities)
- Filtering reduces <5g/cc population from ~2 million to ~350 compositions (CL>0.5, <5$/kg, 5-45at.-%)





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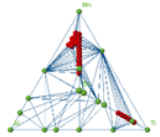

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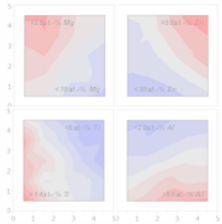

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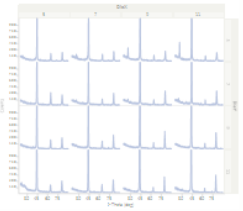

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Small Bulk Samples verification, optimization, tests

Feedback

Large Bulk Samples verification, optimization, tests

Simple Calculated Phase Diagrams show 81% accuracy for database

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- Calculate phase diagram by constructing Gibbs-free energy convex hull
  - Use formation enthalpies for ordered compounds (DFT database), no entropy terms
  - Use solid solution model based on Miedema enthalpy terms and configurational entropy terms
- Results show the highest accuracy for the model with the most terms
- This is complimentary to CALPHAD when databases are not capturing the alloys, and complimentary to DFT calculations when solid solution database not yet available, yet usefulness for wide range of alloys outside of current HEA database (biased towards transition metals) needs to be validated

	Model		TP	FP	FN	TN	ACC
	ΔH	ΔS					
SPSS	M	I	43	103	59	294	0.68
	M	IE	41	89	61	308	0.70
	CE	I	35	32	67	365	0.80
	CE	IE	35	30	67	367	0.81

SPSS = single phase solid solution
TP = true positive
FP = false positive
FN = false negative
TN = true negative
ACC = accuracy (predictability)

ΔH Model:
- M: Miedema model
- CE: Chemical + Elastic interactions

ΔS Model:
- I: Ideal configurational entropy
- IE: Ideal configurational + Excess configurational entropy

T chosen to be 35% T_m CALPHAD, or 43% averaged constituent T_m's when T_m CALPHAD not available

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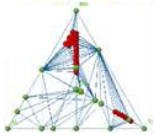

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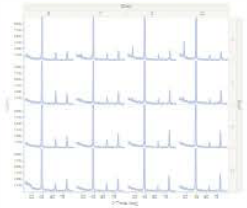

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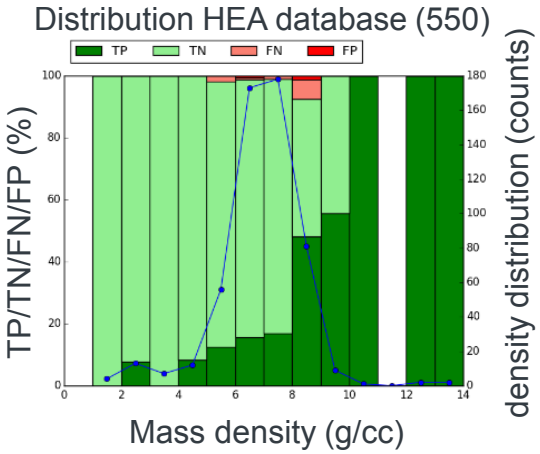
Accuracy by different methods for database 71-82%

- When comparing machine learning to other methods, database reduced from >550 to 45 data points, and 45 points not included to develop machine learning, not to bias comparison towards machine learning
- Where CALPHAD shows 71-77% accuracy for SPSS for the smaller data set (45), it cannot support 30% for larger database (550) where it shows 71-80% accuracy for those (70%) supported by CALPHAD
- HEA database (550) contains very few LDHEA points (almost all not SPSS, and all SPSS <5g/cc by mechanical alloying), so results are potentially biased towards density of 5-9g/cc

SPSS accuracy comparison for different methods with small (45) database

Model	TP	FN	FP	TN	Accuracy
Machine Learning	0.33	0.02	0.16	0.49	0.82
Simple Phase Diagrams	0.31	0.04	0.18	0.47	0.78
CALPHAD-DB1	0.20	0.10	0.13	0.57	0.77
CALPHAD-DB2	0.21	0.10	0.19	0.50	0.71

Sum of TP+FN and sum of TN+FP should be equal for all 4 rows, yet this does not hold for CALPHAD, since not all entries can be run through CALPHAD



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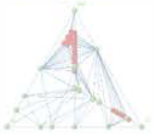

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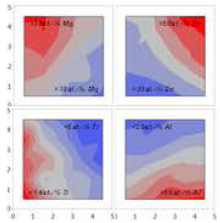

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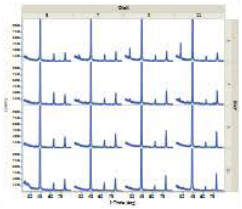

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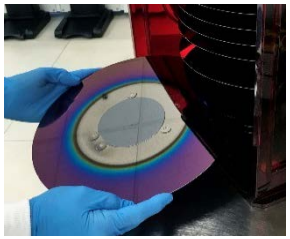
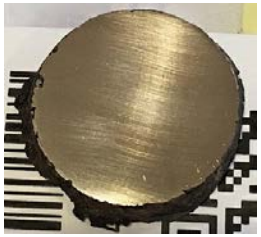
Thin-Film to Bulk Comparison shows good match for XRD

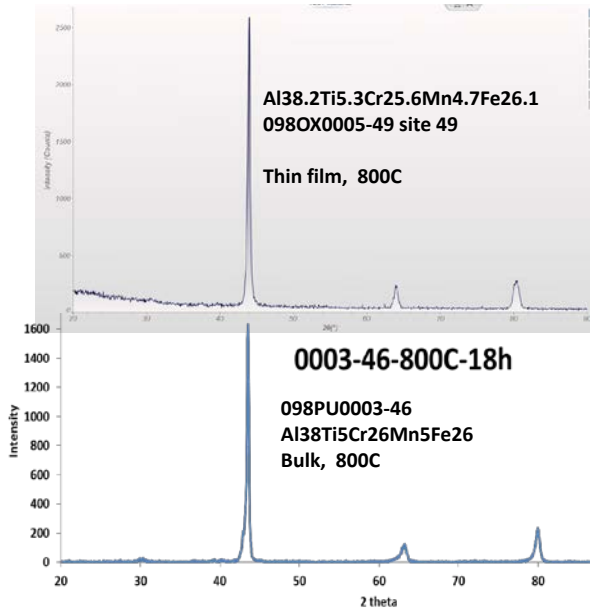
- Known LDHEA proved elusive, so switched to Al-Cr-Fe-Co-Ni for workflow validation
- Demonstrated 100% agreement of crystal structures observed for 21 thin film and bulk samples based on XRD, which includes Al-Cr-Fe-Co-Ni and other 3-e, 4-e, and 5-e alloys
- Hardness map delays HTE screening, since it requires extensive microstructure mapping (grain size, texture, density) to add value to hardness maps, requires additional thin-film processing to ensure valuable results, and extrapolating thin-film hardness values to bulk hardness values for *new* alloys requires *known* parameters for Hall-Petch



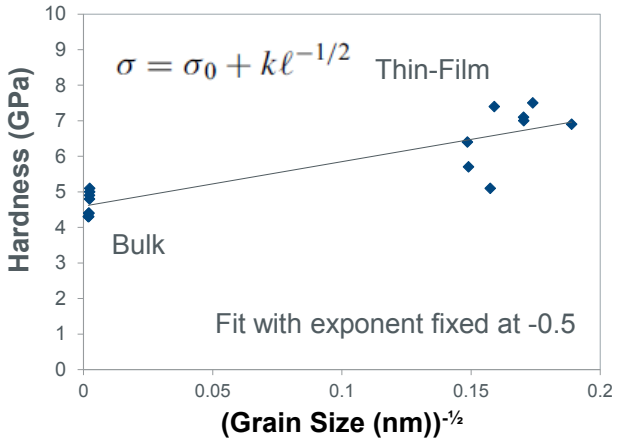
0.5μm-thick gradient film on substrate



0.75”-dia x 0.25”-thick puck for validation



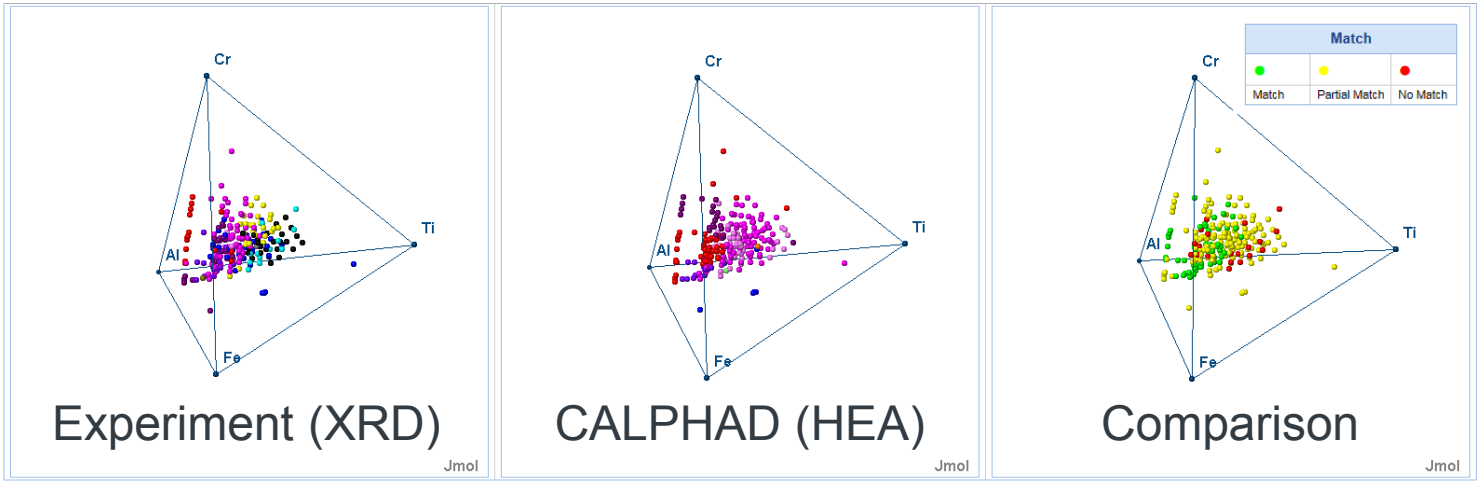
XRD comparison



Hardness comparison

Discrepancy between CALPHAD and experiment for LDHEA

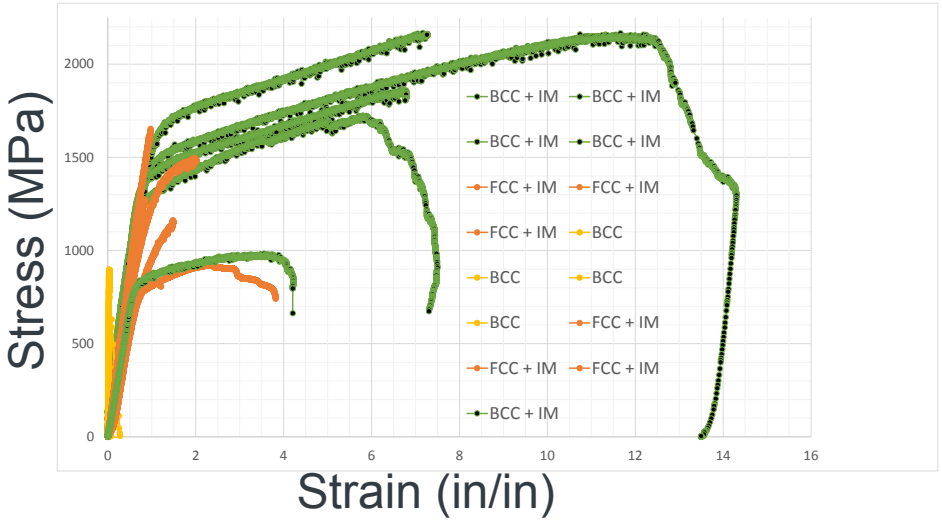
- Note that all relevant binary and/or ternary phase diagrams are not yet assessed in CALPHAD, typically necessary to improve accuracy for quarternary and quinary alloys
- Most CALPHAD work historically went into conventional alloys, not near equiatomic concentrations of e.g. quarternary and quinary alloys
- Experimental results not necessarily 100% equilibrated, and might include errors



Most promising candidates found are 2-phase LDHEA

- *Alloy Design*: Moving from typical visual cut-offs in graphs of phenomenological selection rules to confidence levels based on machine learning shifted the focus from single-phase to multi-phase LDHEA, since machine learning narrowed the number of single-phase LDHEA significantly, in agreement with searches through CALPHAD databases
- *Alloy Design*: Most alloys based on Mg, Al, Si, Ti, Cr, Mn, Fe, Ni, Cu, & Zn
- *Experiments*: Finding viable, ductile candidates moved density above 5g/cc
- *Experiments*: Feasibility of arc melting screened out combination of low boilers mixed with high melters ("ease of manufacturing" filter)
- *Experiments*: VEC rule of limited use to search for FCC-based LDHEA

Room-Temperature Compression (0.5"-dia x 0.75"-long cylinders)



(1) BCC + IM show highest compressive strain
(2) FCC + IM with limited compressive strain
(3) Hard, brittle, single-phase BCC

0.5"-dia x 0.75"-long cylinder under compression

Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year

Collaboration and Coordination with Other Institutions

INTERMOLECULAR

NCSU

- Project Sub
- Produced and characterized small bulk samples

OSU

- Project Sub
- Provided analytical models and phase diagrams

Arconic

- Project Sub
- Produced and characterized bulk alloy samples

GM

- Project Advisor
- Provided guidance on automotive part choice and test protocols

Remaining Challenges & Barriers

- **Mass Density and Cost** – getting below 5.5g/cc and 7$/kg is difficult for ductile FCC/BCC-based LDHEA
- **Modeling** – Validation of new alloy design methods takes time, and relying on existing fast methods often provide evolutionary solutions at best; Difficult to design alloys with predictable mechanical properties
- **Others** – Unknown mechanical properties beyond compressive tests, and transfer from lab to fab

Proposed Future Research

- **Short-term Future Research (balance of 2017): Milestones 2-3 and 2-4**
  - Tensile tests, 25lbs casting, thermo-mechanical process development, and fatigue and corrosion tests
  - Continue to explore 4- and 5-element alloys <5.5g/cc within multinary FCC/BCC-based 4- and 5-element LDHEA
- **Long-term Future Work (follow on work):**
  - Explore more novel microstructures for LDHEA, and focus less on FCC/BCC-based 4- and 5-element LDHEA design
  - Populate and experimentally validate LDHEA database based on Cluster Expansion & Special Quasi-random Structures (CE/SQS)

Any proposed future work is subject to change based on funding levels

Summary Slide

INTERMOLECULAR

Relevance

- Develop a low-density, low-cost, high-strength, concentrated, multinary alloy using HTE

Approach

- Demonstrate correlation between thin-film HTE and bulk alloy properties
- Demonstrate correlation between models and observation
- Identify candidates and test for mechanical properties

Technical Accomplishments

- Validated HTE for LDHEA development
- Developed HT modeling for alloy development
- Achieved SYS = 229MPa x cc/g @ 8$/kg

Future Work

- Tensile/fatigue testing, and optimization
- Single-element substitutions